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Cyclic Oxygen Scavenging Polymers for Barrier Applications

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Cyclic Oxygen Scavenging Polymers for Barrier Applications

by

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Abstract

Cyclic Oxygen Scavenging Polymers for Barrier Applications

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Oxygen scavenging polymers have been shown to improve packaging properties by being incorporated into the matrix of the packaging material by blending, multi-layering, or a combination of both. Addition of a metal salt, photoinitiator, and ultraviolet irradiation to the oxygen scavenging polymer can greatly increase the oxygen scavenging kinetics. The research presented in this report investigates the oxygen uptake and capacity of two polymers with oxidizable pendent rings. The mass uptakes of the cyclic polymers were around 12 wt.% and 17 wt.% and fluctuated some depending on the amount of metal salt (cobalt neodecanoate) was present. It was also found that the cyclic polymers uptook as much as twice the number of oxygen atoms than commercially available 1,4-polybutadiene.

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INTRODUCTION

Many foods, electronics, and pharmaceuticals need to be packaged in materials that restrict oxygen transport from the contiguous environment through the package [1]. Polymers are favored as barrier materials for packaging applications because they are inexpensive, flexible, transparent, and lighter weight than alternatives like glass and metal [2]. Barrier polymer gas transport properties can be further enhanced by incorporating an oxygen scavenging polymer (OSP) into the matrix [3]. The OSP reduces the oxygen transport through the polymer matrix by scavenging oxygen diffusing through the package walls [4].

BACKGROUND

Improving barrier properties in polymers

Conventional packaging polymers can have insufficiently low oxygen permeability to enable their use in high barrier applications [2]. Due to the limitations of these polymers, they are often combined with other materials by blending or multi-layering. For example, a high barrier polymer can be sandwiched between layers of a moderate barrier polymer. By doing so, a thinner layer of the more expensive high barrier material is needed, thus reducing the overall cost and steady state oxygen permeation rate [5]. A combination of both techniques can produce more desirable barrier properties than is achieved by a polymer alone.

Another method to improve polymer barrier properties is to incorporate a reactive species, such as an OSP, into the package film. These materials are known as "active" packaging materials because the OSP, when in the presence of a metal catalyst, will interact with the inside and outside environments of the package wall by reacting with the diffusing oxygen. Figure 1 illustrates this application. By adding 4 wt.% of the OSP, poly(m-xylylene adipamide) doped with cobalt catalyst, to polyethylene terephthalate (PET), the oxygen permeance through the packaging walls can be decreased [6].

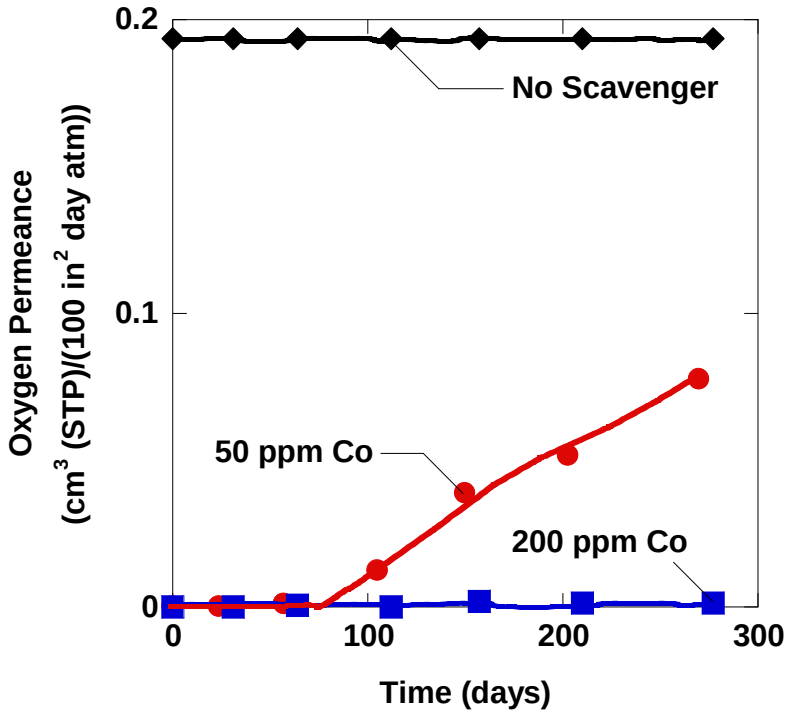


Figure 1: Effect of 4 wt.% scavenger and catalyst loading on oxygen permeance through a layer of PET [6].

Fundamentals of gas transport in polymers

Gas transport through nonporous polymers is most commonly described by the solution-diffusion model [7]. In this model, gas molecules dissolve into the polymer membrane surface at the upstream side, diffuse through the polymer matrix, and then desorb from the surface on the downstream side. The steady state transport of gas *A* through a polymer membrane is expressed by the permeability coefficient, P_A, defined as [8]:

$$P_A = D_A \times S_A \quad (1)$$

Equation (1) suggests that the permeability coefficient is influenced by two terms. The solubility coefficient, S_A, is a thermodynamic term and quantifies the number of gas molecules *A* that dissolve into the membrane. The diffusivity coefficient, D_A, is a kinetic term and characterizes the mobility of gas *A* molecules diffusing through the membrane [8].

Furthermore, permeability can be defined as [8]:

$$P_A = \frac{N_A l}{p_2 - p_1} \tag{2}$$

where N_A is the steady state molar flux of gas *A* through the membrane, l is the membrane thickness, p_2 is upstream pressure of gas *A*, and p_1 is the downstream pressure of gas *A*. The permeability coefficient is most often reported in the literature in units of Barrer, where 1 Barrer is equivalent to 10^{-10} $\frac{\boldsymbol{cm^3(STP)\cdot cm}}{\boldsymbol{cm^2\cdot s\cdot cmHg}}$. Traditionally, barrier polymers have an oxygen permeability less than 6×10^{-3} Barrer, but those with a permeability near 10^{-2} Barrer are often considered adequate [9].

In addition, gas transport through systems consisting of multiple polymers, such as blend and layered systems depicted in Figure 2, can be described. Permeability of blend films, P_{blend}, can be determined from the Maxwell model[10]:

$$P_{blend}=P_c\left[1+3\varphi_d\left(\left[\frac{P_d/P_c+2}{P_d/P_c-1}\right]-\varphi_d\right)^{-1}\right] \quad (3)$$

where φ_d is the volume fraction of the polymer in the dispersed phase, and P_c and P_d are the gas permeability of the continuous and dispersed phase, respectively. Equation (3) is valid for blend films where the dispersed phase is immiscible with the continuous phase [10].

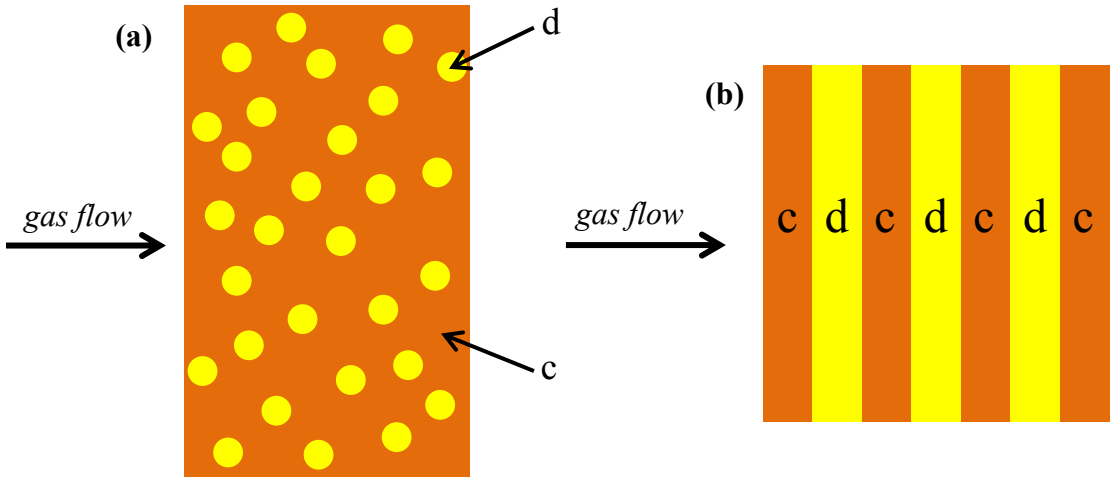


Figure 2: Polymer orientation for (a) blend films and (b) layered films consisting of polymer *c* and *d*.

When polymers are layered continuously with their boundaries clearly defined, like Figure 2b, permeability, P_L, can be described by a series resistance model [10]:

$$\frac{1}{P_L}=\frac{\varphi_c}{P_c}+\frac{1-\varphi_c}{P_d} \quad (4)$$

where φ_A is the volume fraction of polymer *c*, and P_c and P_d are the gas permeability of polymer *c* and *d*, respectively. Equation (4) is valid when the gas flow is perpendicular to the orientation of the layers, as in Figure 2b.

Modeling

Due to the extensive number of experiments associated with characterization of reactive OSPs and the extended time it takes for the experiments to run, modeling provides a reasonable way to predict barrier performance. An accurate model could provide guidance to the ideal composition and morphological structure and reduce the number of experiments that are needed to characterize the performance of a given design.

Models for reactive barrier materials have been developed for homogenous films [11], polymer blends [12, 13], and multilayered homogenous films [14] with butadiene-containing polymers as the reactive species. Numerical solutions to the models revealed three time regimes for the flux of oxygen: early, intermediate, and late [11]. In blend films, a "shrinking core" model approximates the kinetics of the OSP oxidation process when the reaction is much faster than the diffusion [12, 13]. For multilayer alternating inert and reactive films, the model showed multiple inflection points during the intermediate time regime that corresponded with the number of reactive layers [14]. The author concluded that the best OSP configuration for a selected set of inert and reactive materials depends strongly on the diffusion and solubility properties of the materials [14].

Project objectives

The purpose of this project is to systematically characterize the oxygen scavenging capabilities of selected OSPs. Oxidation capacity and kinetics were determined through mass uptake experiments, and permeation experiments were used to measure the gas transport properties of the films. Melt-processable conditions and formulations that retain the scavenging capacity and kinetics of OSPs after being incorporated into blend or layered structures need to be established. Analyzing the oxidized structures of the OSPs will help determine a plausible oxidation mechanism. Using the experimental results obtained, modeling efforts can be validated and improved. This project will aim to study OSPs in dense, blended, and layered films.

Two OSPs were chosen for this project based on their ability to scavenge oxygen. Past polymers that have been studied include polybutadienes and block copolymers containing butadiene [15, 16]. Unfortunately, their oxidized structures are known to break down and release low molar byproducts that could potentially migrate into the packaged product [3]. To avoid the release of byproducts upon oxidation, polymers with oxidizable pendent rings were selected.

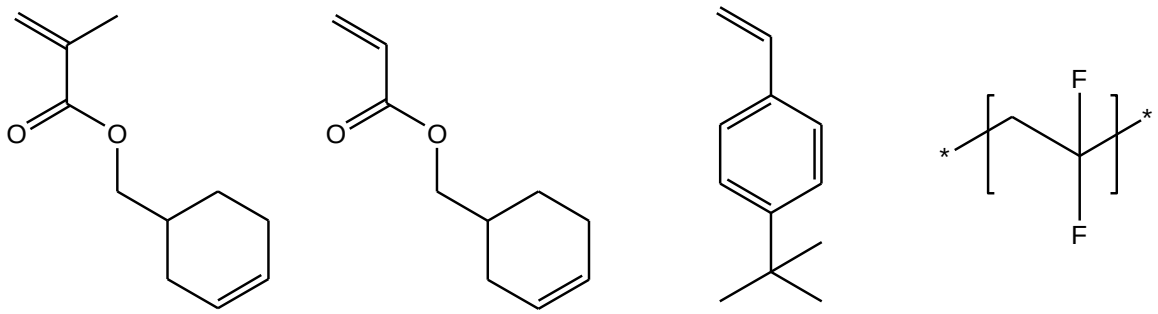
In blend films, the chemical reaction needs to be fast relative to the diffusion [1]. To slow down the diffusion of oxygen, the matrix polymer should be relatively impermeable and already have decent oxygen barrier properties. To increase the reaction rate of oxygen by the dispersed OSP, copolymerization of the reactive polymer with a

polymer which has a lower oxygen permeability will decrease the overall permeability of the OSP. The OSP should have a similar or lower oxygen permability than that of the matrix so passing oxygen will readily diffuse into the OSP [5]. Without the copolymerization with a more permeable polymer, the passing oxygen will avoid the OSP altogether, and none of the oxygen will be absorbed by it.

EXPERIMENTAL

Materials

The OSP monomers used in this study are cyclohexenylmethyl methacrylate (CHMA) and cyclohexenylmethyl acrylate (CHAA) (Figure 3a and b). These monomers were chosen because their vinyl double bond allows for polymerization, and the double bond in the pendent ring provides beta hydrogens for oxidation. *p*-tert-Butylstyrene (tBS) monomer was chosen to copolymerize with the OSP monomers because of its high free volume (Figure 3c). Polyvinylidene fluoride (PVDF) was selected for the matrix because it is relatively impermeable and melt-processable at temperatures under 300°C (Figure 3d).



(a) (b) (c) (d)

Figure 3: (a) cyclohexenylmethyl methacrylate (CHMA) (b) cyclohexenylmethyl acrylate (CHAA) (c) *p*-tert-butylstyrene (tBS) (d) polyvinylidene fluoride (PVDF).

Catalyst selection

The transition metal chosen as the oxidation catalyst for this project is cobalt as it has been shown to be the most effective in catalyzing oxidation [17]. Cobalt is readily available as a carboxylic acid salt which is highly soluble in hydrocarbons, so it can be easily added to the scavenging polymer [17]. Furthermore, it has been shown that cobalt salts with long-chain fatty acids are particularly effective at catalyzing oxidation in unsaturated polymers [18]. Therefore, the cobalt salt selected for this project is cobalt neodecanoate, shown in Figure 4.

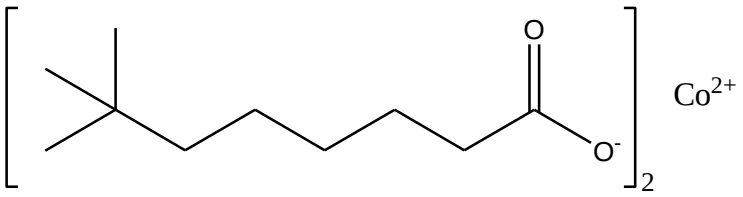


Figure 4: Structure of cobalt neodecanoate.

Synthesis

The polymers used in this study were synthesized via bulk, free radical polymerization. Homopolymers of CHMA and CHAA were polymerized using azobisisobutyronitrile (AIBN) as the initiator. The monomer was added to a 30 mL test tube along with 0.5 to 1 wt % AIBN. Nitrogen was bubbled through the solution for approximately 30 minutes, and then the test tube was placed in a 65°C water bath for 30 minutes for CHMA and 1 hour for CHAA. The polymer solution was precipitated in

methanol yielding a polymer powder. The homopolymers were then dried in a vacuum oven at 60°C overnight.

The copolymers used in this study were also synthesized via bulk free radical polymerization. Predetermined compositions of (tBS) and either CHMA or CHAA were added to a 30 mL test tube along with 0.5 to 1 wt % AIBN. Nitrogen was bubbled through the solution for approximately 30 minutes, and then the test tube was placed in a 65°C water bath for 2 hours. The viscous copolymer solution was precipitated in methanol yielding a powder. The copolymer was dried in a vacuum oven overnight at 60°C. NMR and FTIR analysis of the copolymers and homopolymers indicate that the copolymers have both monomers in its structure.

Film Casting

Oxygen scavenging films were made by spin coating. PolyCHMA was dissolved in toluene in a 25 mL bottle to make a 5 wt % solution. Predetermined amounts of benzophenone photoinitiator and cobalt neodecanoate solution, also dissolved in toluene, were added to the polymer solution. The bottle was wrapped in foil so that the benzophenone would not prematurely initiate while in solution. Once the added components were dissolved, the solution was filtered through a 0.45 μm Whatman® PURADISCTM Teflon syringe filter. The filtered solution was used to cast thin films onto a silicon wafer using a spin coater at 1000 RPM for 60 seconds. These films were approximately 600 nm thick.

Melt Extrusion

Kynar® 760 grade of PVDF was received from Arkema. The PVDF was processed in a twin screw DSM micro-compounder (Xplore®, The Netherlands) under an inert nitrogen atmosphere to determine its processing conditions, such as its temperature and residence times. The melt-processed PVDF is made using a film die and cooled with nitrogen gas while it is collected on an uptake roller. Defect free films of Kynar® 760 PVDF were produced at 250°C with mixing speeds of 150 RPM for 15 minutes. While the PVDF is being collected on the rollers, the mixing speed is slowed to 50 RPM for better extrusion control.

Oxygen Uptake

Oxygen scavenging films made via spin coating were activated using a UV light source at 365 nm. Since silicon wafers are impermeable to gases, films were left on the wafer and activated on only one side. The films containing benzophenone photoinitiator were activated with 12 J/cm^2 of energy using the UV light source to begin oxidation. The UV light source was stored in a glove bag with an inert nitrogen atmosphere to prevent premature oxidation during the activation period. Once the film had been activated, the wafer was removed from the glove bag, and its mass was recorded over time. During the experiment, films were kept in a 35°C oven in ambient air with Drierite™ to keep the humidity low. Oxygen mass uptake, M_t, was calculated as the difference between the

mass of the film at some given time, m_t, and the film's initial mass at the start of the oxidation, m_0:

$$M_t = m_t - m_0 \tag{5}$$

FTIR was used to determine qualitatively whether the film underwent oxidation by comparing the homopolymer spectrum to that of the oxidized homopolymer.

PRELIMINARY RESULTS

Thin film oxidation

Thin film oxidation studies were performed on polyCHMA and polyCHAA homopolymers with thicknesses between 600 and 1000 nm. Past oxidation studies on polybutadiene by Li et. al. showed that the mass uptake rate in thin films (thicknesses less than 10 μm) is limited by the oxidation kinetics rather than the diffusion of oxygen through the film [19]. Figure 5 shows the oxidation of polyCHMA films doped with various levels of cobalt catalyst at 35°C and activated with 12 J/cm^2 of UV irradiation. The amount of catalyst has an effect on the oxidation kinetics of polyCHMA, particularly the induction period associated with the 50 ppm and 200 ppm samples. It is even worth noting that the 50 ppm sample has very similar kinetics to the 0 ppm sample, indicating that 50 ppm cobalt loading has little effect on the oxidation kinetics. In general, the higher the cobalt concentration, the faster the oxidation uptake occurs.

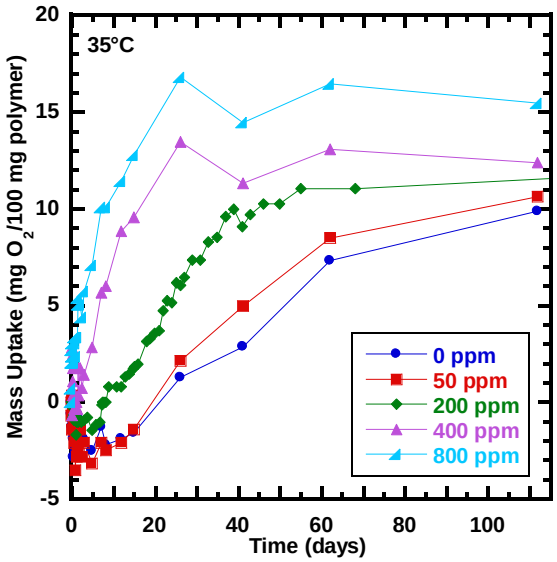


Figure 5: Oxidation of polyCHMA films at 35°C doped with 0, 50, 200, 400, and 800 ppm cobalt catalyst and activated with 12 J/cm^2 UV irradiation.

Figure 6 shows the oxidation of polyCHAA at 35°C with various cobalt catalyst loadings. PolyCHAA appears to have no induction period in the samples with low levels of cobalt catalyst, though there does appear to be a slight decrease in the uptake kinetics between the 200 ppm and 50 ppm samples. The sample with 0 ppm cobalt catalyst has an induction period of approximately 25 days before it eventually uptakes similar amounts of oxygen as the samples containing catalyst. Compared with polyCHMA, polyCHAA oxidizes faster and more easily when doped with a cobalt catalyst, and requires lower concentrations of cobalt catalyst to begin uptake.

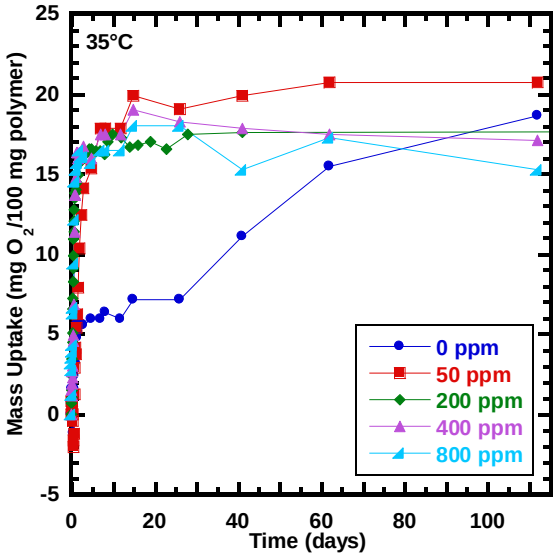


Figure 6: Oxidation of polyCHAA films at 35°C doped with 0, 50, 200, 400, and 800 ppm cobalt catalyst and activated with 12 J/cm^2 UV irradiation.

One method used to quantify the capacity for oxygen uptake is calculating the theoretical oxygen uptake. Theoretical oxygen uptake can be calculated using the following equation:

$$\text{Theoretical Oxygen Uptake} = \frac{\text{MW oxygen atom(s)}}{\text{MW repeat unit}} \times 100\% \qquad (6)$$

For polyCHMA, the molecular weight of the repeat unit is approximately 180, so if one CHMA repeat unit were to react with one oxygen atom, the mass uptake would be 8.9 wt.%, which is lower than the maximum observed in the experimental data of polyCHMA in Figure 5. But if one CHMA repeat unit were to react with two oxygen atoms, the mass uptake would be 17.8 wt.%, which is a little higher than the observed maximum uptake in Figure 5. Therefore, it appears the polyCHMA is uptaking between one and two oxygen atoms.

The theoretical oxygen uptake can also be calculated for polyCHAA using Equation (6). The molecular weight of the polyCHAA repeat unit is 166, so if one CHAA repeat unit reacts with one oxygen atom, the mass uptake would be 9.6 wt.%. If one CHAA repeat unit reacts with two oxygen atoms, the mass uptake would be 19.3 wt.%. From Figure 6, the polyCHAA appears to be taking up a mass of 17-20 wt.% which is closer to the mass that corresponds with two oxygen atoms. It is possible that some water molecules are being absorbed into the polymer film as well.

Comparison with 1,4-polybutadiene

The oxidation of polyCHMA and polyCHAA was compared with 1,4-polybutadiene studied by Li et. al. [19] Similar oxidation conditions were mimicked to Li's studies with slight variations in the film thicknesses. Figure 7 shows the oxygen uptake of the three films in terms of mass (A) and moles (B). In Figure 7A, the 1,4-polybutadiene uptakes almost twice as much mass as polyCHAA with nearly the same initial uptake kinetics. Compared with polyCHMA, 1,4-polybutadiene uptakes closer to three times as much mass. However, when converted to a molar basis as shown in Figure 7B, the 1,4-polybutadiene uptakes 1 oxygen atom per repeat unit, while polyCHMA and polyCHAA uptake 1.5 and 2 oxygen atoms per repeat unit, respectively. While 1,4-polybutadiene uptakes a substantially larger mass than polyCHMA and polyCHAA, only one oxygen atom is scavenged even though there are two sites for oxygen attachment per repeat unit.

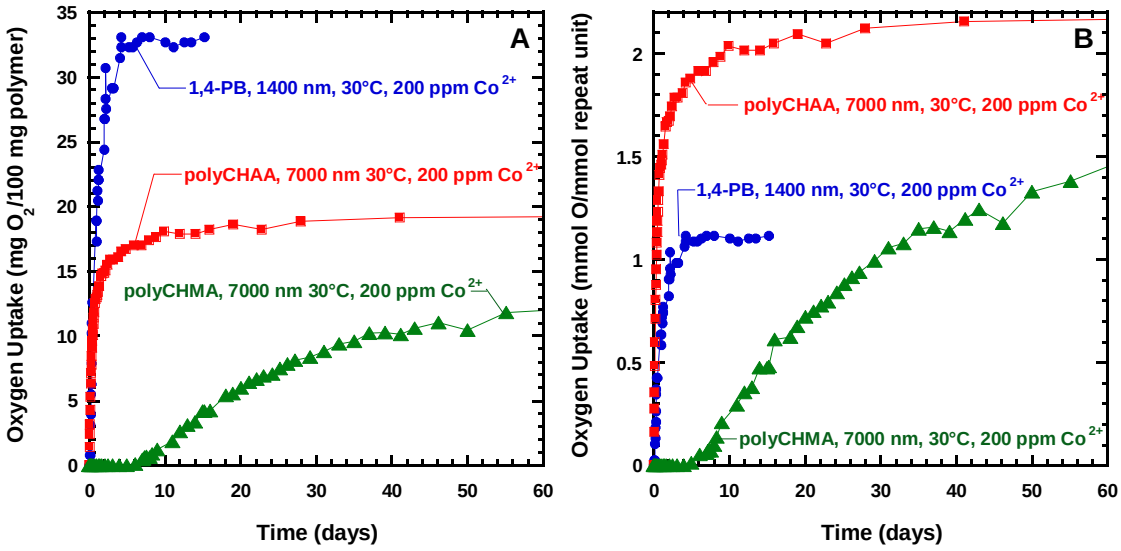


Figure 7: Comparison of oxygen uptake capacity of 1,4-polybutadiene (1,4-PB), polyCHMA, and polyCHAA. 1,4-PB data from Li et. al. [19]

FTIR analysis

FTIR analysis was used to confirm polymerization of CHMA and CHAA monomers and oxidation in polyCHMA and polyCHAA films. Figure 8 shows the FTIR analysis of CHMA. The disappearance of the vinyl double bond peak at 1640 cm^{-1} confirms polymerization of the monomer. The broad peak observed at 3450 cm^{-1} in the oxidized film is associated with bonded hydroxyl groups, indicating that a chemical change had occurred. The carbonyl peak at 1740 cm^{-1} becomes broadened in the oxidized polymer film which may indicate that some of the oxidized sites are converting to carbonyl groups in addition to the hydroxyl groups.

Figure 9 shows the FTIR analysis of CHAA, and the same conclusions were drawn.

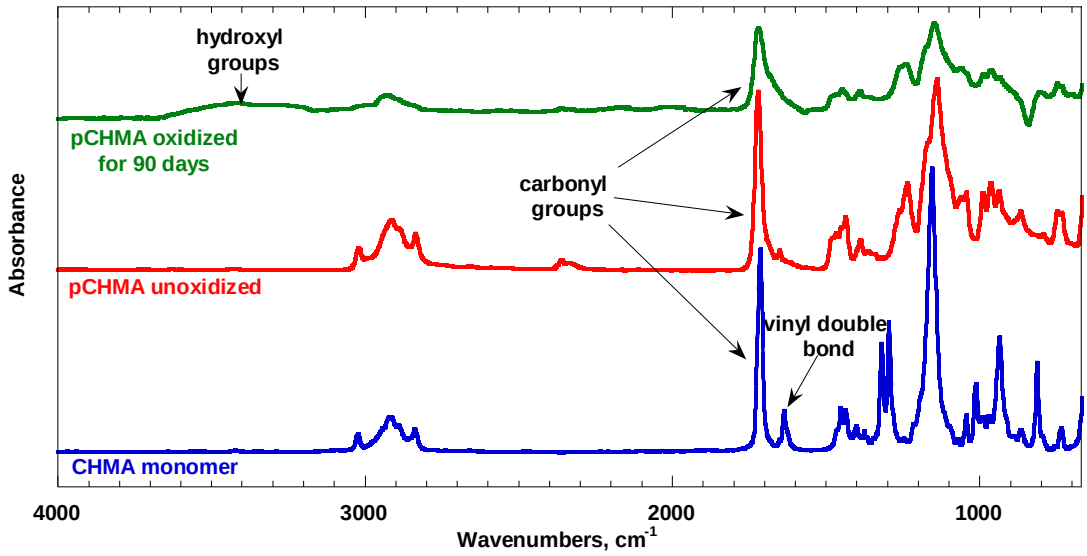


Figure 8: FTIR spectra of CHMA monomer, unoxidized polyCHMA, and oxidized polyCHMA.

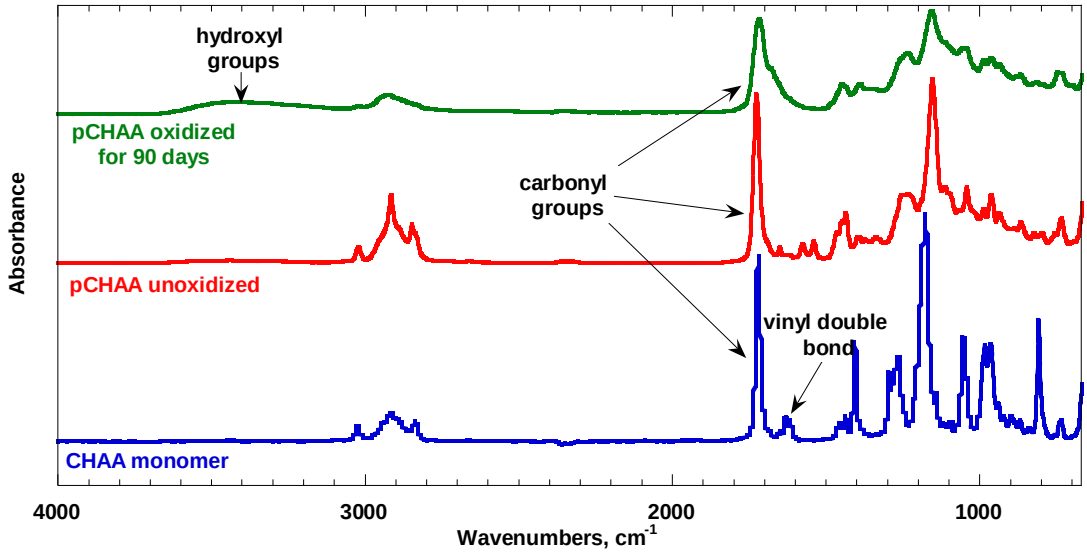


Figure 9: FTIR spectra of CHAA monomer, unoxidized polyCHAA, and oxidized polyCHAA.

Poly(CHMA-co-tBS) and poly(CHAA-co-tBS) copolymers were successfully synthesized via free-radical polymerization. FTIR analysis of the copolymers and

respective monomers was used to confirm that both monomer units were present in each copolymer and the spectra are shown in Figure 10 and Figure 11. The carbonyl peak near 1740 cm^{-1} from polyCHMA and polyCHAA also appears in the respective copolymer spectra. The peak at 820 cm^{-1}, which is characteristic of 1,4-disubstituted aromatics, appears in both the polytBS and copolymer spectra.

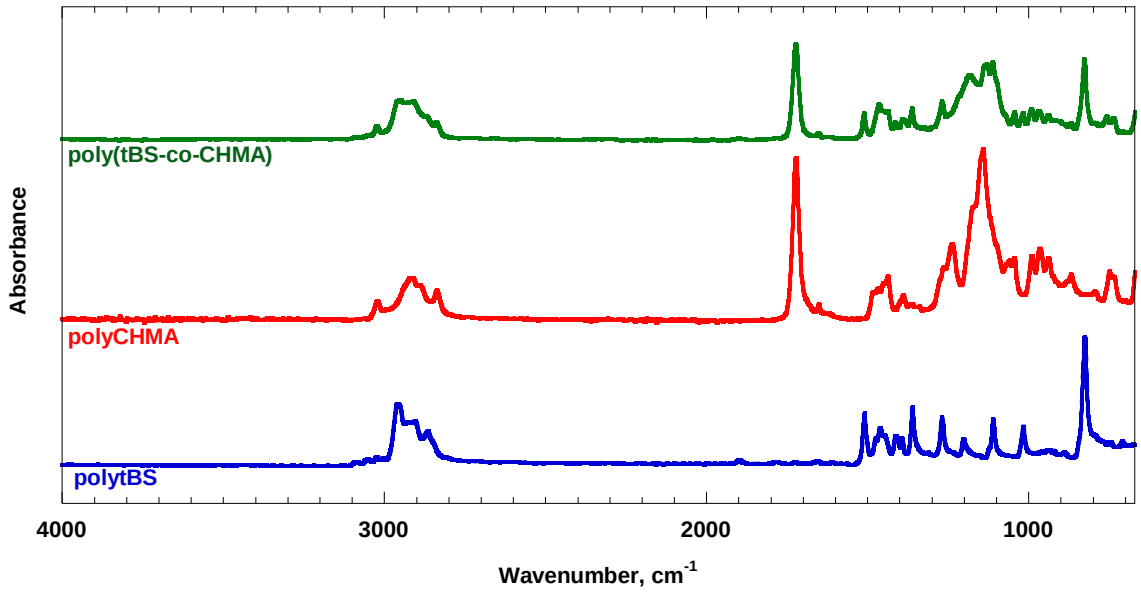


Figure 10: FTIR spectra poly(tBS-co-CHMA), polyCHMA, and polytBS.

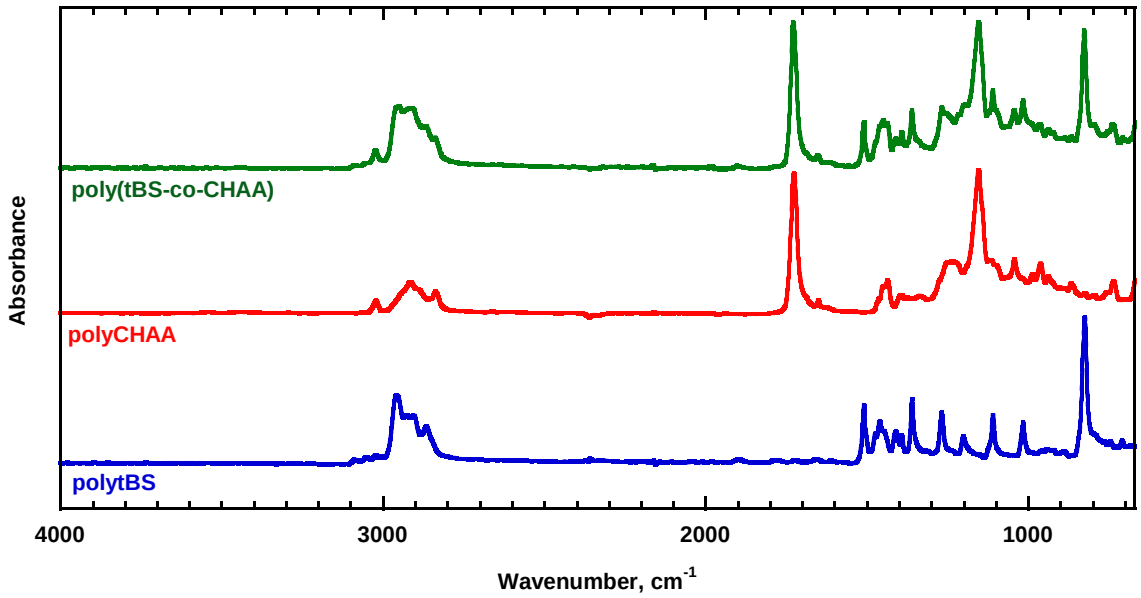


Figure 11: FTIR spectra of poly(tBS-co-CHAA), polyCHAA, and polytBS.

CONCLUSIONS AND FUTURE WORK

PolyCHMA and polyCHAA appear to be promising oxygen scavenging polymers as they both uptake atmospheric oxygen. In the presence of a cobalt catalyst, the oxygen uptake rate in thin films can be increased by increasing the cobalt concentration, up to 800 ppm. Compared to 1,4-polybutadiene, polyCHMA and polyCHAA uptake more oxygen atoms per repeat unit and therefore have more capacity. However, due to the large molar mass of the polyCHAA and polyCHMA repeat units, the oxygen uptake comprises a very small weight fraction of the repeat units. One possible reason for the ability of polyCHAA and polyCHMA to uptake more oxygen is that the cyclic ring on the repeat unit opens the structure up allowing more stability when an oxygen atom attaches.

For future studies, it would be beneficial to the literature to have permeation data of oxygen, nitrogen, and carbon dioxide for polyCHMA and polyCHAA, using nitrogen as an inert, non-oxidizing gas molecule to determine the transport properties at various stages of oxidation without the film undergoing further oxidation. Confirmation of the oxidation end structures of polyCHMA and polyCHAA using solid state NMR would help in understanding the oxidation mechanism for these homopolymers.

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